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13. ABSTRACT (Maximum 200 words)

Experimental methods were developed to study the chemical kinetics of NF(X³Σ⁻), NF(a¹Δ), and NF(b¹Σ⁺) molecules in a gas phase flow reactor. Since the F + NCO and F + N₃ reactions were used to produce the NF(X) and NF(a) molecules, respectively, experiments also were done to characterize N₃ and NCO radicals by laser induced fluorescence. With the exception of the halogens, most stable molecules quench NF(b) by a physical, E → V quenching mechanism. In contrast, the NF(a) state seems to interact with most molecules by a chemical mechanism. Neither NF singlet state is highly reactive at room temperature, and NF(a) and NF(b) are good molecules for energy storage. The interaction of NF(a) with I₂, ICl and IF resembles that for O₂(a¹Δ). The first step is rapid E → V transfer, which is followed by utilization of a second NF(a) molecule giving I atoms. The concentrations of NF(a) and NF(b) were monitored by their fluorescence intensities. The NF(X) concentration was observed by the N₂(A) + NF(X) excitation-transfer reaction.

14. SUBJECT TERMS

NF(X³Σ⁻), NF(a¹Δ), NF(b¹Σ⁺), reaction rates, metastable states, energy storage,
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FINAL REPORT

A. INTRODUCTION

The AFOSR grant supported two postdoctoral assistants, Drs. Kangyan Du and Sanjay Wategaonkar, for full time study of the chemistry of $NF(X^3\Sigma^-, a^1\Delta$ and $b^1\Sigma^+)$. We coupled our work closely with other laboratories studying $NF(a,b)$ as an energy storage system. This Final Report describes completed work by listing the published papers. The work that is complete, but not yet published, will be described in narrative form. During the grant period, we moved our laboratory from Willard Hall to a new Chemistry building. Sanjay put considerable effort into constructing a totally new flow reactor, installing a Nd:YAG-laser pumped dye-laser, and interfacing a new LeCroy digitizer to a PC computer. The dye-laser system plus digitizer provides an excellent probe for monitoring reactive intermediates. Kangyan rebuilt his $NF(a)$ and $NF(b)$ flow reactors in the new laboratory. This required less effort because the detection techniques are just $NF(a)$ and $NF(b)$ fluorescence. This new construction has provided excellent facilities and instrumentation for continued new work on $NF(X,a,b)$ or other molecules with similar energy storage properties.

While waiting for the Nd:YAG-laser to be installed, Sanjay did a study of the $N_2(A) + OH$ excitation-transfer reaction (item 3 in the reference list). This reaction has good potential as a chemical monitor for $[OH]$. Sanjay's major experimental effort was to develop the $2F + HNCO$ reaction system as a source for $NCO(X)$ and $NF(X)$ radicals. That work has been completed and this chemical system was used to investigate the chemistry of $NCO(X)$ and $NF(X)$. Sanjay also characterized the products, mainly $NCO + F$, from the reaction of CO with $NF(a)$.

Dr. Du's work provides a definitive study of the chemistry of $NF(a)$. The rate constants for self-quenching and for quenching by a wide range of stable molecules and reactive atoms have been published. The quenching by halogens, ICl and IF was especially interesting, because he demonstrated that IF gave E-V transfer without generating I atoms. On the other hand, I_2 and ICl gave E-V transfer with generation of I atoms from secondary reactions. One manuscript describing quenching by $NF(X)$, NF_3 , NF_2 and N_2F_4 remains to be published. In addition to the $NF(a^1\Delta)$ work, Dr. Du developed an improved source of $NF(b)$, which generates ~50 times higher concentration than the $Ar(^3P_{0,2}) + NF_2$ reaction used previously by this laboratory. The

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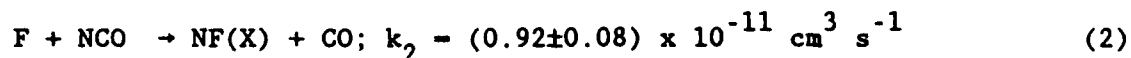
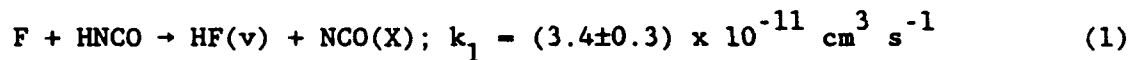
apparatus that Dr. Du built is now available to measure the temperature coefficients for a few quenching reactions with NF(a). Doing such a study for NF₂ and F atoms is especially important for practical applications utilizing NF(a).

In the following pages a summary will be given for the 2F + HNC reaction system. A short description also will be given for the unpublished results of NF(a) interacting with molecules containing NF bonds. These descriptions are followed by a listing of the published papers.

B. THE 2F + HNC REACTION SYSTEM

Introduction

The F atom reaction with HNC is a good source of NCO radicals, as well as ground state NF radicals, in a flow reactor. In order to do quantitative kinetic studies, it is necessary to know the rates and stoichiometry of the generating reactions. The system is adequately described by (1) and (2) with the listed rate constants.



The rate constant for reactions (1) and (2) were determined by monitoring [NCO] via laser-induced fluorescence as a function of [F] and reaction time. The F + HNC reaction had been qualitatively investigated previously by Du and Setser as a source of NF(X) radicals. They estimated the rate constant for reaction (2) as $\sim (5 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ from the NCO(A-X) fluorescence intensity, which was excited by N₂(A) in the reaction system. The rate constant for HF formation from reaction (1) had been previously determined as $4.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ by comparing the HF(v=1) infrared chemiluminescence to that from the F + CH₄ reaction. There was a large uncertainty in this value, however, since the HF(v=0) population was not measured. The $4.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ value is based on a linear surprisal estimate for the HF(v=0) distribution. The combination of earlier work and the present study based on monitoring [NCO] shows that (1) and (2) are the only important reactions



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in the F/HNCO system, providing that the $[NCO]$ and $[NF(X)]$ are low enough that bimolecular radical-radical reactions are unimportant.

Experimental Method

Experiments were done in a 5 cm diameter, 80 cm long, halocarbon wax coated Pyrex flow reactor pumped by a combination Roots blower plus mechanical pump. Due to the slow reaction rates, most of the experiments were done under conditions of reduced flow velocity at 3 Torr pressure. The reactor was fitted with baffle arms and quartz observation windows for doing LIF measurements. The entrance of the reactor was fitted with a microwave discharge tube for producing F atoms from a CF_4/Ar mixture. A movable inlet was provided for adding HNCO at different positions in the reactor. The reaction time between F and HNCO could be varied by adjusting the distance between the inlet and the LIF zone. Another reagent inlet was placed immediately before the observation zone. This inlet was used to add a monitoring reagent (5% C_2H_6 in Ar) for F atom titrations (using the $F + CF_3I$ reaction).

HNCO was prepared by the reaction of steric acid with HNCO and purified by distillation before being stored as a 5% mixture in Ar. The Ar carrier gas was standard industrial grade that passed through commercial traps to remove hydrocarbons and O_2 and finally through liquid- N_2 cooled molecular sieve traps to remove H_2O . Most other reagents were purchased from Matheson or PCR, Inc.

The F atom concentration was determined by titration with CF_3I for each experiment. The HF(3-0) emission from the $F + C_2H_6$ reaction at 890 nm was used to monitor the $[F]$ as a function of the titrant (CF_3I) concentration. The end point of the titration was determined by extrapolating the $I(HF)$ vs $[CF_3I]$ plot to zero HF intensity. Alternatively, the $[F]$ was determined by fitting the observed $I(HF)$ vs $[CF_3I]$ profile by numerical integration of the rate equations.

Laser-induced fluorescence was used to monitor the NCO radical concentration using the $NCO(A-X)$ transition. A Lambda Physik dye-laser was pumped by the third harmonic of a Nd:YAG (Quintel International, Model YG661s-30) laser. The dye-laser was tuned to the (000-000) transition in the $NCO(A-X)$ band system at 438.5 nm and the resulting fluorescence was collected using a photomultiplier and filter assembly. The fluorescence waveform was recorded using a digitizer interfaced to a personal computer.

The time integrated LIF intensity was used to measure the relative NCO(X) concentration.

Experimental Results

The results from LIF monitoring of [NCO] strongly suggest that reactions (1) and (2) adequately describe the $F + \text{HNCO}$ reaction system. Du and Setser's previous observation of NCO(A-X) chemiluminescence from the F/HNCO reaction system can be explained by the presence of N atom impurity, which reacts with NCO to generate $\text{N}_2(\text{A})$. Metastable $\text{N}_2(\text{A})$ subsequently excites NCO(A) by an excitation-transfer reaction. It is necessary to control the impurities in the Ar carrier gas that might lead to the generation of N, O and H atoms in the microwave discharge. Also, sufficient time is needed to allow the second reaction to go to completion to generate [NF(X)] from a known [HNCO].

Depending upon the choice of $[F]_0$ vs $[\text{HNCO}]_0$, the $2F + \text{HNCO}$ reaction system is an adequate source for both NCO(X) and NF(X) in a flow reactor. By choosing conditions such that $[F]_0 \leq [\text{HNCO}]_0$, a known concentration of [NCO] can be generated. Then another reagent can be added downstream at variable time to react with NCO. The [NCO] can be monitored under pseudo-first order conditions and rate constants for removal of NCO by the added reagent can be measured. Alternatively, excess $[F]_0$ can be used, then all of the [HNCO] is converted to NF(X) and reactions with this known [NF(X)] can be studied.

We also used LIF to probe for the nascent NCO(X) vibrational distribution from reaction (1). There is a very small degree of excitation in the bending and asymmetric stretch modes. However, the $\langle f_v(\text{NCO}) \rangle$ is less than 0.10, which is consistent with a direct H-atom abstraction reaction. Thus, the $F + \text{HNCO}$ reaction is characterized by $\langle f_v(\text{HF}) \rangle = 0.3-0.4$ and $\langle f_v(\text{NCO}) \rangle = 0.10$; the remaining energy probably is released as relative translational energy. The $\langle f_v(\text{HF}) \rangle$ is uncertain because the $\text{HF}(v=0)$ has not been assigned.

In order to demonstrate the utility of this source for systematic studies of reaction rates of NCO, we investigated several reactions of NCO with stable molecules at room temperature. The rate data were well behaved and the rate constants given in Table 1 were obtained under pseudo first-order decay rate conditions for [NCO]. The reaction with NO was selected

for comparison of our data with other rate constants in the literature. The agreement was found to be satisfactory. As might be anticipated, the NCO radical is readily removed by unsaturated molecules. However, the rate constants vary widely and there is a correlation with the ionization energy of the reagent molecule, which implies an addition mechanism. The reactions with NO and NO₂ are relatively rapid, but the reaction with O₂ is slow. The reaction rate for H abstraction from H₂S was too slow to measure, but abstraction can be observed with HI. The NCO(X²Π) radical is not a very reactive radical at 300K. This work will be published in the J. Phys. Chem. in the near future.

Table 1 - Summary of the 300K rate constant measurements for NCO(X)

Reagent	Ionization energy; eV	Rate Constant	
		10 ⁻¹¹	cm ³ sec ⁻¹
C ₄ H ₆	9.08	2.4±0.1	
C ₃ H ₆	9.75	1.1±0.1	
C ₂ H ₄	10.50	0.12±0.1	
C ₂ H ₂	11.40	0.019±0.002	
NO	9.27	3.1±0.2	
NO ₂	9.80	0.75±0.05	
HI		0.57±0.03	
H ₂ S		< 1.0 x 10 ⁻³	
O ₂		< 1.0 x 10 ⁻³	

C. QUENCHING RATE CONSTANTS OF $\text{NF}(a^1\Delta)$ BY N_2F_4 , NF_3 , NF_2 , $\text{NF}(\text{X})$, SiF_4 , HNCO
AND $\text{NCO}(\text{X})$ AT ROOM TEMPERATURE

Introduction

The quenching rate constants of $\text{NF}(a^1\Delta)$ by a series of stable molecules and a few reactive atoms have been reported previously from this laboratory using the flow reactor technique. The $2\text{F} + \text{HN}_3$ reaction was used as the source of the metastable $\text{NF}(a)$ molecule. The mechanisms for quenching of $\text{NF}(a)$ by stable molecules can be divided into two broad categories: those proceeding by chemical reaction and those giving physical deactivation to $\text{NF}(\text{X})$. The magnitude of the rate constants for molecules in the first category correlated with the basicity of the reagents that could act as Lewis bases and with the ionization energy of the unsaturated molecules. The quenching constants for atoms normally considered to be reactive have a wide range of values, but $\text{NF}(a)$ is not especially reactive toward open-shell species. The physical quenching channel has been documented only for the interaction of $\text{NF}(a)$ with I_2 , ICl and IF .

Since $\text{NF}(a^1\Delta)$ probably would be generated by the $\text{H} + \text{NF}_2$ reaction in practical devices, there is a need to know the quenching rate constant by NF_2 and likely precursors to NF_2 , such as NF_3 and N_2F_4 . These quenching rates are slow at room temperature and, therefore, difficult to measure in a flow reactor. However, we attempted these measurements in order to establish lower limits to the rate constants. These experiments were done in a glass reactor and the reactions of the reagents with the walls could generate some SiF_4 . Therefore, the quenching of $\text{NF}(a)$ by SiF_4 also was examined. The quenching constants and mechanisms for $\text{NF}(a^1\Delta)$ interacting with itself and with $\text{NF}(\text{X}^3\Sigma^-)$ and $\text{NF}(\text{b}^1\Sigma^+)$ are also of practical interest. These reactions involve the ground and/or excited state potentials of N_2F_2 , which should be amenable to theoretical treatment. We used the $2\text{F} + \text{HNCO}$ reaction system to generate $\text{NF}(\text{X})$. The chemical environment is complex, but reduction of $[\text{NF}(a)]$ was observed for high $[\text{NF}(\text{X})]$, and an estimate of the rate constant for removal of $\text{NF}(a)$ was made. Since HNCO and NCO were in the flow reactor for the $\text{NF}(\text{X})$ experiment, we also examined the rates of their reactions with $\text{NF}(a)$. No attempt was made to study the $\text{NF}(a) + \text{NF}(\text{b})$ reaction.

The $[\text{NF}(a)]$ was generated by the $2\text{F} + \text{HN}_3$ reaction using known $[\text{F}]_0$ and $[\text{HN}_3]_0$. Fortunately there is now a consensus about the rate constants of

the primary and secondary reactions. However Dagidigan and co-workers recently identified HNF as a product from the $F + \text{HN}_3$ reaction. The branching fraction for N_3 vs. HNF is not established, but we will continue to use our prior assignment that $[\text{NF(a)}] = 0.85 [\text{HN}_3]_0$ for excess $[F]_0$. The reagent of interest was added to the reactor section of the flow tube and the decay of $[\text{NF(a)}]$ was observed by monitoring the NF(a-X) fluorescence as a function of time for fixed reagent concentration or as a function of reagent concentration at fixed reaction time. It was not possible to search for products from the quenching reactions in the present study.

Experimental Methods

The apparatus and techniques used to generate NF(a) and to measure quenching rate constants of NF(a) by stable molecules has been described in previous publications. In this study, a 150 cm long and 6.4 cm diameter Pyrex tube coated with halocarbon wax served as the flow reactor. The carrier gas, Ar, was purified by passing the gas through a commercial trap (Matheson 6406) and cooled (196 K) molecular sieve filled traps before being introduced into the reactor. The pressure in the reactor was monitored by a transducer gauge (MKS). A mechanical pump, 1500 L min^{-1} , provided a flow speed of 650 cm s^{-1} at 2-4 Torr pressure. The NF(a) molecules in the concentration range of 10^{11} - $10^{12} \text{ molecule cm}^{-3}$ were produced in the pre-reactor by the $2F + \text{HN}_3$ reaction. The F atoms were generated by passage of a 30% CF_4/Ar mixture, together with additional Ar, through a microwave discharge. The F atoms and HN_3 flows were introduced at the front of the reactor, and the $F + \text{N}_3$ reaction was complete by the time the flow reached the reagent inlet, which was placed 28 cm downstream from the HN_3 inlet. Experiments generally were conducted for $[\text{NF(a)}] < 1 \times 10^{12} \text{ cm}^{-3}$ in order to minimize the importance of the bimolecular self-destruction rate.

The inlet port for the quenching reagent was placed 28 cm downstream from the HN_3 inlet of the pre-reactor. The reagent flow line was covered by heating tape to permit thermal dissociation of N_2F_4 into NF_2 . The reagent concentration in the reactor was obtained from the flow rates and the total pressure. The flow rates for the stable reagent molecules were measured by observing the pressure rise in a 5 liter vessel. The NF_2 flow rate was assigned as twice the measured N_2F_4 flow, since the N_2F_4 was completely dissociated by heating the line to 500K. The heating tape on the reagent

line extended as close as possible to the connection to the main reactor to prevent the loss of NF_2 from recombination on any cold surface. The concentration range for NF_2 in the reactor was 0.4 to 2.4×10^{15} molecule cm^{-3} . For a NF_2 recombination rate constant of 1.3×10^{-32} cm^6 molecule $^{-2}$ s^{-1} , the loss of $[\text{NF}_2]$ from the homogenous three-body recombination reaction must be considered for our reaction times of ~ 100 ms. Therefore, the rate equations for the NF(a) quenching by NF_2 and N_2F_4 were numerically integrated with the NF_2 recombination included in the model to obtain the NF(a) quenching rate constant for NF_2 .

The NF(X) molecules were generated by reactions of F atoms with HNCO in the pre-reactor as described in the first pages of this report. Since the formation rate of NF(X) is 5 times slower than the formation rate of NF(a) from $\text{F} + \text{N}_3$, the HNCO was introduced into the pre-reactor using the flow line normally employed for HN_3 , in order to have as long a reaction time for $\text{F} + \text{NCO}$ as possible. The NF(a) , from $2\text{F} + \text{HN}_3$, was added to the reactor via a separate miniature pre-reactor that was attached to the inlet normally used for the quenching reagent. The miniature pre-reactor was 18 cm long and 2 cm in diameter and had a 15 - 20 ms reaction time. Excess $[\text{F}]_0$ was used in both pre-reactors to drive the $\text{F} + \text{NCO}$ and $\text{F} + \text{N}_3$ reactions to completion. The $[\text{NF(a)}]$ and $[\text{NF(X)}]$ in the main reactor were based on the measured HN_3 and HNCO flow rates and the $[\text{F}]_0$.

The HNCO was prepared from the reaction of steric acid with potassium cyanate under vacuum at 358K. The raw product collected in a trap at 77 K contained CO_2 , as well as the HNCO . The CO_2 was removed by distilling the sample through a trap maintained at 163 K with dynamic pumping. The distilled sample was examined by infrared absorption spectroscopy and found to be free of CO_2 . Because a significant fraction of the HNCO polymerizes in the condensed phase, a large part of the HNCO sample was consumed by the purification process. A 1% HNCO/Ar mixture was prepared from the pure sample and stored in a 12 Pyrex glass container and metered to the reactor. Freshly prepared HNCO/Ar mixtures were employed for the NF(X) experiments in order that the $[\text{HNCO}]$ would be reliable.

The SiF_4 , NF_3 and N_2F_4 tanks were obtained from Ozark-Mahoning Inc., Matheson, and Hercules, respectively. Samples were taken from the tanks and purified by freeze-thaw-pump cycles before being loaded into reservoirs attached to the gas handling system. We found that several freeze-pump-thaw

cycles were necessary for purification of the N_2F_4 , since the N_2F_4 sample contains N_2 (and perhaps F_2). These three reagents were stored in reservoirs without dilution, since high concentrations were needed to observe quenching of $NF(a)$.

The detection system was 0.5 m Minuteman monochromator, equipped with a 500 nm blaze grating (1200 grooves mm^{-1}) and a cooled photomultiplier tube (Hamamatsu R-942-02). The monochromator was placed on a table that could be moved along the reactor for observation of the emission after a given reaction time.

Experimental Results

Since the bimolecular self-destruction rate is small, the differential law for the decay of $NF(a)$ in the presence of added reagent with concentration $[Q]$ is given by the eq. below.

$$\frac{d[NF(a)]}{dt} = -(k_1[Q] + k')[NF(a)]$$

The quenching rate constant is k_Q and k' is the sum of all other first order rate constants for removal of $NF(a)$. Providing that the glass surface is coated with wax, quenching at the wall is slow and k' is negligible. The integrated rate law has the simple form given by $\ln I_a = -(k_Q[Q] + k')t + A$, where I_a is the intensity of the $NF(a-X)$ emission observed at 850 nm. The radiative lifetime, 5-6 s, is short enough to permit observations of the emission intensity, but long enough that radiative decay is not important for our reaction times < 0.1 s. The semilog quenching plots of the $NF(a-X)$ intensity versus added $[NF_3]$ and $[SiF_4]$ are shown in Figure 1 for the longest feasible reaction times that could be used. Slopes of the plots are products of the quenching rate constant and the reaction time. The apparent reaction coefficients of NF_3 and SiF_4 with $NF(a)$ are $(1.6 \pm 1.0) \times 10^{-17}$ and $(1.4 \pm 0.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, if no correction is made for back diffusion. High Ar flows were used in order to maintain a large total pressure and as large a dilution factor as possible for the NF_3 and SiF_4 . Even though the throttling valve was nearly closed to increase the reaction time, the quenching by NF_3 was barely observable for the maximum $[NF_3]$. In fact, the observed change in $[NF(a)]$ with the addition of NF_3 might be attributed to other effects, such as back diffusion and turbulence from the large flow of added NF_3 .

The rate constant reported for NF_3 is based only upon one measurement, because we did not want to use large quantities of NF_3 , which is rather

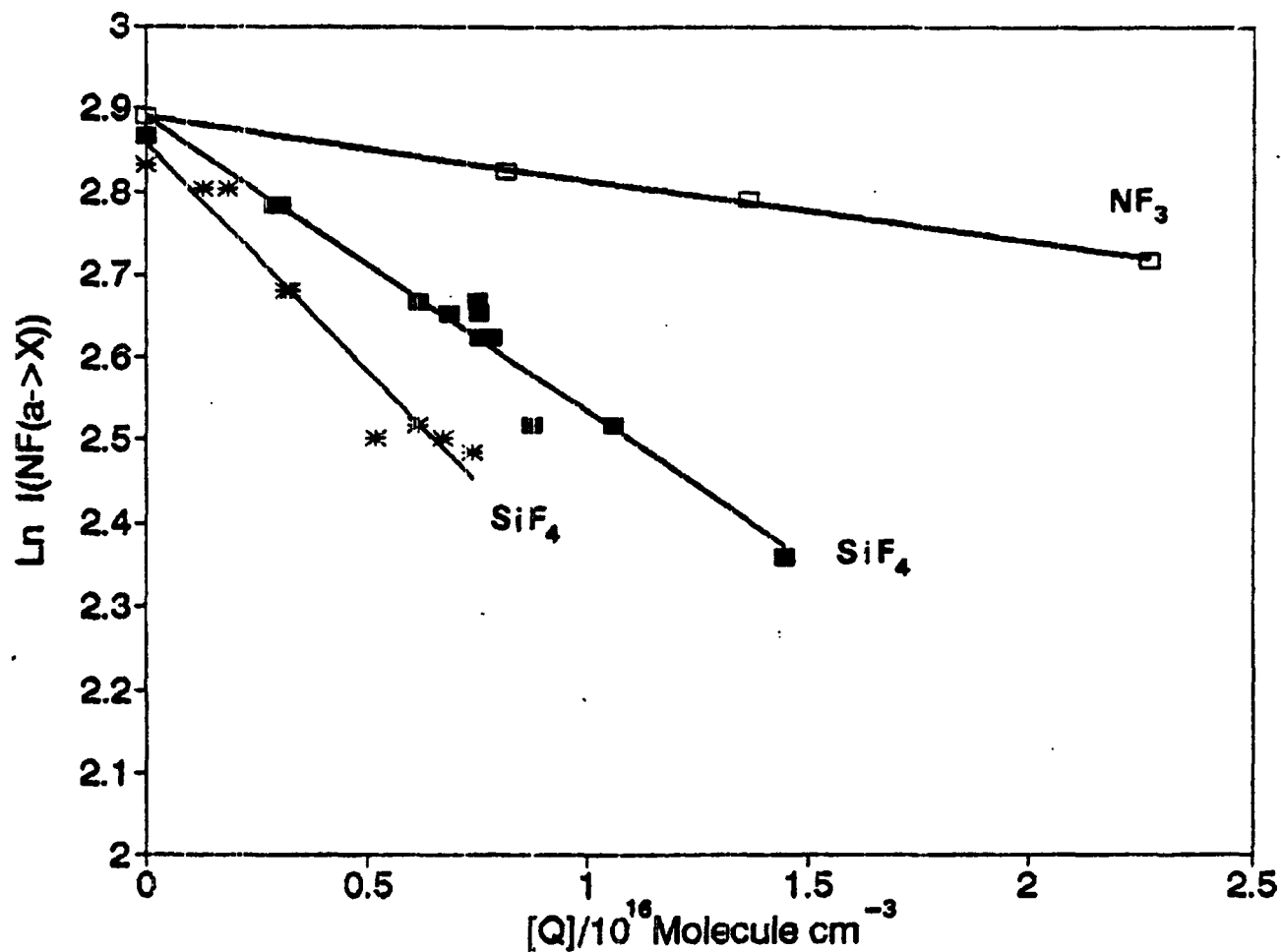


Figure 1. First order quenching plot for NF_3 and SiF_4 . The $[\text{HN}_3]_0$ and $[\text{F}]_0$ were 1.4×10^{12} and 6.8×10^{12} molecules cm^{-3} , respectively, $\Delta t = 0.46$ s and the pressure was 8.8 Torr for the NF_3 experiment. The $[\text{HN}_3]_0$ and $[\text{F}]_0$ were 1.1×10^{12} and 5×10^{12} molecule cm^{-3} , respectively, with $\Delta t = 0.31$ s (■) and 1.2×10^{12} and 5×10^{12} molecule cm^{-3} , respectively, with $\Delta t = 0.50$ s (*) and the total pressure was 6.5 Torr for the SiF_4 experiments.

expensive. This value of k_{NF_3} is five times smaller than the one reported in earlier work, which also should have been reported as an upper limit because very little reduction in $[\text{NF(a)}]$ was observed for the range of $[\text{NF}_3]$ used in that experiment. We favor the smaller value reported here, which is assigned as an upper limit to the true quenching rate constant at 300K. The SiF_4 reaction rate also is very slow, but reduction in $[\text{NF(a)}]$ was observed. The two sets of data shown in Figure 1 should provide a realistic measure of k_{SiF_4} ($(1.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$). Since the reagent concentrations were high, impurities could cause the measured decay constants to be upper limits to the true rate constants for NF_3 and SiF_4 .

The reaction of NF(a) with N_2F_4 was studied for various conditions and reaction times to obtain a reliable rate constant. Daily degassing of the N_2F_4 sample was necessary, since N_2F_4 slowly decomposes into N_2 and F_2 . The rate constants obtained from the longer reaction times, 0.2-0.3 s, are in good agreement with those obtained from the shorter reaction times, 0.1-0.2 s, and $k_{\text{N}_2\text{F}_4}$ is assigned as $(4.0 \pm 1.0) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. Since similar rate constants were obtained for different conditions, the N_2F_4 rate constant should be reliable to within 25%, at least for this sample of N_2F_4 . The rate constant is approximately 200 times larger than for NF_3 .

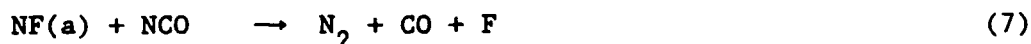
The NF_2 was introduced into the flow reactor by thermally dissociating the N_2F_4 by heating the flow line to 500K. To avoid recombination on the cold surface of the narrow (8 mm diameter) inlet tube, the heating tape extended to the connection with the main reactor. Upon heating the N_2F_4 flow, a reduction in the degree of quenching of NF(a) always was observed. Thus, k_{NF_2} must be smaller than $k_{\text{N}_2\text{F}_4}$. However, the proper $[\text{NF}_2]$ for the relatively long reaction times must be evaluated carefully in order to obtain a value for k_{NF_2} from the observed decay of the $[\text{NF(a)}]$.

Because of the relatively small rate constant, large $[\text{NF}_2]$ and long reaction times were necessary to observe a substantial decay of $[\text{NF(a)}]$. Since the rate constant for three-body recombination of NF_2 in Ar is $1.3 \times 10^{-32} \text{ molecule}^{-2} \text{ cm}^6 \text{ s}^{-1}$, a significant fraction of the $[\text{NF}_2]$ recombines to N_2F_4 for reaction times of 80-120 ms in 2.3 Torr of Ar. Thus, the following reactions must be considered in evaluating the data.



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important result is the qualitative observation that NF(a) is not rapidly removed by NF(X) concentrations of $3-6 \times 10^{12}$ molecule cm^{-3} and that $k_{\text{NF(X)}}$ must be smaller than the NF(a) bimolecular self-quenching rate constant. The kinetic model below was used to assign a quenching rate constant to NF(X).



In the first analysis we assumed physical quenching for the deactivation of NF(a) by NF(X), so the [NF(X)] was augmented by the quenching. Another possibility would be (6a) with formation of $\text{N}_2 + 2\text{F}$, which would reduce [NF(X)]. The differential rate law for the decay of NF(a) is given as:

$$-\frac{d\text{NF(a)}}{dt} = k_B[\text{NF(a)}]^2 + (k_F[\text{F}] + k_{\text{NF(X)}}[\text{NF(X)}] + k_{\text{NCO}}[\text{NCO}])[\text{NF(a)}]$$

Since the F atom concentration was high, quenching by F atoms was explicitly included, although the degree of quenching by F atoms actually is minor. The NCO reaction also was explicitly included, although the initial NF(X) concentration was always higher than the NCO concentration. Fitting the data gave $k_{\text{NF(X)}} = (3.5 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. In the second set of calculations, formation of N_2 and 2F by (6b) was assumed. Now the best fit result gave a rate constant of $(2.5 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. This mechanism gives a somewhat smaller value because the [NF(X)] is not enhanced and because F atoms are generated. We can not distinguish between the two, therefore, an average rate constant of $(3.0 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ was selected for reaction (6). The rate constant for quenching of NF(a) by NF(X) seems to be an order of magnitude smaller than the self-quenching constant, k_B .

The quenching of NF(a) by HNCO and NCO was studied by the fixed point method. The NF(a) molecules were generated in the large pre-reactor by the usual $2\text{F} + \text{HN}_3$ reaction and the HNCO was introduced into the main reactor at the reagent inlet. Because a large amount of the 1% HNCO in Ar mixture was needed to obtain observable quenching, only a few experiments with the HNCO/NCO system were conducted. Because of the presence of excess F atoms from the pre-reactor for reaction times of 76 and 143 ms, some of the

HNCO was converted to NCO and even to NF(X) for low [HNCO]. Therefore, the observed reduction in [NF(a)] was related to rate constants for HNCO and NCO by running a computer simulation model that included all the relevant reactions. For the larger flow rates of HNCO most of the quenching is from NCO and HNCO. By combining the two sets of data, estimates for k_{NCO} and k_{HNCO} were obtained; see Table 2. Since the experimental quenching curves do not show any obvious strong dependence on the nominal [HNCO], the k_{NCO} and k_{HNCO} values must not be too different from each other and from $k_{\text{NF(X)}}$.

The measured rate constants are summarized in Table 2 and are compared to other studies from the literature. The most important point is that the rate constants for N_2F_4 , NF_3 , NF_2 and NF(X) are small at 300K. There is a degree of disagreement on the best value for NF_2 and N_2F_4 , and further work is needed. It does seem clear that $k_{\text{NF}_2} < k_{\text{N}_2\text{F}_4}$ from our work, and most likely k_{NF_2} is close to $1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 300K. Since the reaction with NF_2 probably is chemical in nature and gives $\text{N}_2 + 3\text{F}$ as products, this rate and its temperature dependence has important practical implications. These results will be discussed in more detail in the published paper, item 10 of the publication list.

TABLE 2 - Quenching Rate Constant of NF(a¹Δ) at Room Temperature.

Reagent	This work $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Other studies $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
NF(X)	30 ± 10	
NF_2	0.16 ± 0.04	$0.09^e; 0.027 \pm 0.010^d$
N_2F_4	0.40 ± 0.10	0.012 ± 0.001^c
NF_3	$\leq 0.0016 \pm 0.0010$	0.0074 ± 0.0007^c
SiF_4	$\leq 0.014 \pm 0.005$	
HNCO	70 ± 20	
NCO	45 ± 15	

- (a) The self-quenching constant of NF(a) is $5 \pm 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- (b) The quenching rate constant by F atoms is $4 \pm 2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$; this rate constant was used for the kinetic models to obtain $k_{\text{NF(X)}}$, k_{NCO} and k_{HNCO} .